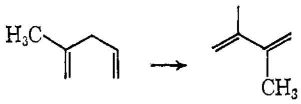
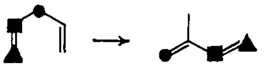
The reaction of 2-methyl-1,4-pentadiene gave 2,3-dimethyl-1,3-butadiene (26%) and *trans*-2-methyl-1,3-pentadiene (24%) at 54% conversion, as isomeric products.



(5)

The results from these experiments indicate that each carbon with its label assumes the position in the product as described in eq 6. These data effectively eliminate a number of mechanistic possibilities from consideration. They require a reaction path that can account for the transfer of hydrogen to and from carbons originally present in a terminal vinyl group in the 1,4-diene precursor. They are entirely consistent with a mechanism that would involve the intervention of a cyclopropylcarbinylmetal derivative.[1b]



(6)

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(11) (a) Petroleum Research Fund Predoctoral Fellow, 1969; (b) NDEA Predoctoral Fellow, 1965–1968.

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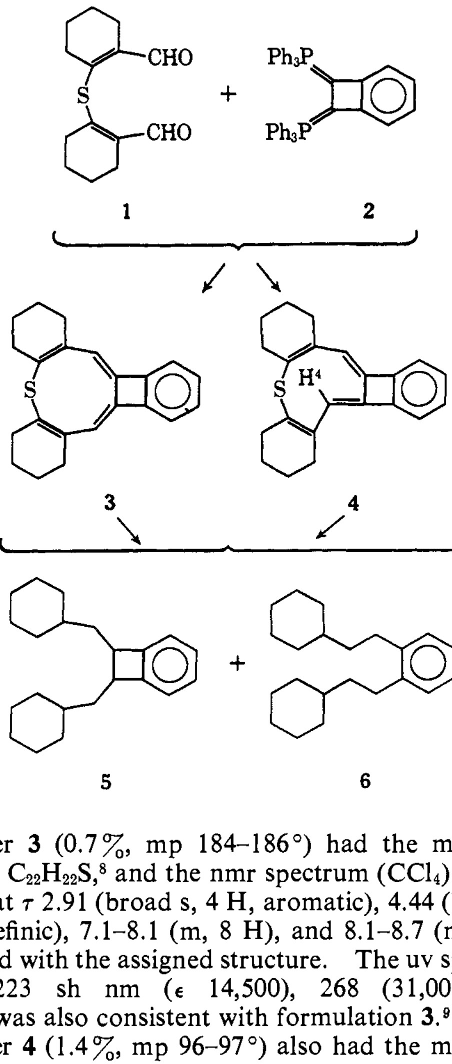
The Synthesis of Benzo[3,4]cyclobuta[1,2-*e*]dicyclohexeno[*b,h*]thionin, an Analog of Biphenylene Containing a Thionin Ring

Sir:

We report the synthesis of two isomers of benzo[3,4]cyclobuta[1,2-*e*]dicyclohexeno[*b,h*]thionin (**3**, **4**), analogs of biphenylene[1] in which one of the benzene rings has been replaced by an alkylated, potentially aromatic thionin ring.[2] Isomer **4** is also of interest in that it represents the first isolated case of a fully unsaturated nine-membered-ring system containing a *trans* double bond.[3]

A solution of 2,2′-thiodi-1-cyclohexene-1-carboxaldehyde (**1**)[6] in tetrahydrofuran was added to an equimolar solution of preformed 1,2-bis(triphenylphosphoranyl)benzocyclobutene (**2**)[7] in ether under nitrogen at room temperature. Chromatography on alumina gave a mixture (*ca.* 1:2) of **3** and **4**, and these compounds were then separated by preparative tlc on alumina.



Isomer **3** (0.7%, mp 184–186°) had the molecular formula $C_{22}H_{22}S$,[8] and the nmr spectrum (CCl_4) showed signals at τ 2.91 (broad s, 4 H, aromatic), 4.44 (broad s, 2 H, olefinic), 7.1–8.1 (m, 8 H), and 8.1–8.7 (m, 8 H), in accord with the assigned structure. The uv spectrum [λ_{max}^{EtOH} 223 sh nm (ϵ 14,500), 268 (31,000), 375 (6200)] was also consistent with formulation **3**.[9]

Isomer **4** (1.4%, mp 96–97°) also had the molecular formula $C_{22}H_{22}S$,[8] and the nmr spectrum (CCl_4) showed signals at τ 2.92 (broad s, 4 H, aromatic), 4.17 (broad s, 1 H, olefinic), 4.38 (broad s, 1 H, olefinic), 7.3–7.9 (m, 8 H), and 7.9–8.6 (m, 8 H). This spectrum reveals that the two olefinic protons are nonequivalent, indicative of the mono-*trans* structure **4**. The signal at τ 4.38 is assigned to H-4, since the solvent dependence of the position of this signal differs from that observed for the olefinic protons in **3**, whereas the signal at τ 4.17 has a similar solvent dependence.[10] The uv spectrum of **4** [λ_{max}^{EtOH} 224 sh nm (ϵ 17,800), 285 sh (6600), 314 (11,400)] differs considerably from that of **3** and other 1,2-dimethylenebenzocyclobutenes,[9] presumably

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(1) For the synthesis of other biphenylene analogs, see (a) M. P. Cava, K. Narasimhan, W. Zeiger, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, **91**, 2378 (1969); (b) C. S. Baxter, P. J. Garratt, and K. P. C. Vollhardt, *ibid.*, **91**, 7783 (1969); (c) P. J. Garratt and K. P. C. Vollhardt, *Chem. Commun.*, 109 (1970).

(2) The only previously known thionin derivative is 4,5:6,7-dibenzothionin: A. P. Bindra, J. A. Elix, P. J. Garratt, and R. H. Mitchell, *J. Amer. Chem. Soc.*, 90, 7372 (1968).

(3) The existence in solution at low temperatures of the mono-*trans*-cyclononatetraenyl anion[4] and probably also of mono-*trans*-oxonin[5] has recently been reported.

(4) G. Boche, D. Martens, and W. Danzer, *Angew. Chem., Int. Ed. Engl.*, 8, 984 (1969).

(5) S. Masamune, S. Takada, and R. T. Seidner, *J. Amer. Chem. Soc.*, 91, 7769 (1969).

(6) M. Weissenfels and M. Pulst, *Tetrahedron Lett.*, 3045 (1968).

(7) A. T. Blomquist and V. J. Hruby, *J. Amer. Chem. Soc.*, **89**, 4996 (1967).

(8) Satisfactory elemental analyses and mass spectral data have been obtained for all new crystalline compounds.

(9) The uv spectra of all of the 1,2-dimethylenebenzocyclobutene derivatives examined by us show a high-wavelength maximum above 325 nm.

(10) The olefinic proton signals in **3** move downfield in CD_2Cl_2 and C_6D_6 as compared to CCl_4, whereas H-4 in **4** is unchanged in CD_2Cl_2 and moves upfield in C_6D_6.

due to the configurational change induced by the *trans* double bond.

The fact that **3** and **4** differ only in the stereochemistry is supported by the results of Raney nickel desulfurization. Treatment of **3** in refluxing ethanol wtih a large excess of Raney nickel gave a mixture (~2:1) of **5** (*m/e* 296) and **6** (*m/e* 298) in 50% yield. Similar desulfurization of **4** led to a mixture (~4:1) of **5** and **6** in 40% yield, the identity of the compounds being established by glc and mass spectral comparison.

Oxidation of **3** with 6% hydrogen peroxide in acetic acid gave the sulfoxide **7** (67%, mp 252–254°), characterized by molecular composition[8] and spectral properties. Similar oxidation of **4** gave **8** (40%, mp 190–193°).[8] The nmr spectrum (CCl_4) of **7** showed signals at τ 2.91 (broad s, 4 H, aromatic), 4.26 (broad s, 4 H, olefinic), 6.8–7.7 (m, 8 H), and 7.7–8.8 (m, 8 H), and that of **8** had signals at τ 2.90 (broad s, 4 H, aromatic), 4.02 (broad s, 1 H, olefinic), 4.15 (s, 1 H, olefinic), and 7.0–8.8 (m, 16 H). The signal at τ 4.15 in **8** is assigned to H-4, again on the basis of solvent dependence.[10] The uv spectrum of **7** [λ_{max}^{EtOH} 267 nm (ϵ 37,700), 359 (8000)] is that expected for a 1,2-dimethylenebenzocyclobutene derivative,[9] whereas that of **8** [λ_{max}^{EtOH} 225 nm (ϵ 16,500), 315 (9500)] resembles **4**.

3

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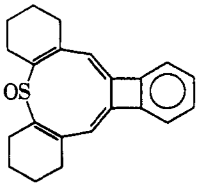
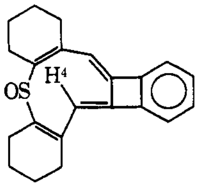


7

4

↓



8

The nmr spectra of both **3** and **4** clearly indicate that these compounds do not have delocalized, aromatic thionin rings, but that this system has a buckled, nonplanar conformation. The absence of delocalization in these systems is further supported by the finding that the chemical shifts of the aromatic protons are virtually unaltered when **3** or **4** is oxidized to the corresponding sulfoxide, in contrast to the behavior of 2-thianorbiphenylene on oxidation.[1c] The properties of **3** and **4** suggest strongly that thionin, like oxonin,[5,11] is not an aromatic system.[12]

Acknowledgments. One of us (A. B. H.) thanks the Shell Company of Australia for a Postgraduate Scholarship, and we are also indebted to the Royal Society (London) for generous financial support.

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[12] On the other hand, azonine appears to have some aromatic character: A. G. Anastassiou and J. H. Gebrian, *Tetrahedron Lett.*, 825 (1970).

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Photochemical and Thermal Reactions of Tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dien-9-one[1]

Sir:

The decarbonylation of cyclic unsaturated ketones by irradiation or heating has been studied experimentally by several investigators and also discussed from a theoretical point of view.[2] Examples are the photochemical decarbonylation of cyclohepta-3,5-dienone[3] and 7,8-benzobicyclo[4.2.1]octa-2,4,7-trien-9-one[4] and the thermal decarbonylation of norbornadienone,[5] a dimer of cyclopentadienone[6] and tropones.[7] In connection with such decarbonylation of cyclic unsaturated ketones, we have studied the photochemically and thermally induced reactions of tricyclo-[3.3.1.$0^{2,8}$]nona-3,6-dien-9-one (I)[8] and have discovered that I behaves in a sharply contrasting manner in the two processes.

When I was irradiated in tetrahydrofuran or carbon tetrachloride using a high-pressure mercury lamp (Toshiba H 400-p), a clean reaction occurred to give a single oily product (II). The product was confirmed as cyclooctatetraene on the basis of its nmr spectrum, showing a singlet at τ 4.26, and formed an adduct, mp 170°,[9] with maleic anhydride. Neither sensitizing nor quenching effects were observed when the irradiation was carried out in the presence of benzophenone, fluorenone, anthracene, or piperylene. The decarbonylation also took place by irradiation with filtered 307-nm light,[10] where I has an absorption maximum due to $n-\pi^*$ excitation. These facts indicate that the photoreaction of I proceeded *via* the $n-\pi^*$ singlet state and that cyclooctatetraene (II) did not originate from semibullvalene (uv max in ethanol 225–235 nm, sh) which was considered to be a possible intermediate resulting from the decarbonylation of I.[11] In addition, no ester was formed by irradiation of I in methanol and no effect was observed when I was irradiated in the presence of a radical scavenger such as 2,6-di-*t*-butylphenol or toluene.

In contrast with such a lability to light, I was so stable to heat that attempted pyrolysis through a quartz column heated at 200° resulted in its complete recovery. However, upon pyrolysis at 500° I afforded two oily products, III and IV, in 28 and 26% yields, respectively, with the recovery of I in a 26% yield. The

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